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Ordered Structures of Molecular Bottlebrushes

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In this review 'molecular bottlebrushes' are flexible polymers densely loaded with equally flexible side chains. Interest in these structures arises from the possibility of lyotropic behaviour in dilute solution in a good solvent, as well as the possibility of highly ordered microphase-separated states in the melt. In addition, supramolecular chemistry has led to alternative and often much simpler ways of synthesizing complex polymer architectures. Here we will concentrate on molecular bottlebrushes obtained by hydrogen bonding between homopolymers and end-functionalized oligomers, and address their complex phase behaviour. Particular attention will be given to the possibility of lyotropic behaviour and to the role of the reversibility of the noncovalent bonding. The coupling between micro- and macrophase separation and the possibility of various Lifshitz points will also be discussed.

The phrase 'molecular bottlebrush' will be reserved for flexible polymers with a large number of equally flexible side chains linked covalently or noncovalently to the polymer backbone. In recent years exciting new routes to complex copolymer architectures have been developed. It has been shown that nitroxide-mediated 'living' free-radical polymerization can be used to control the macromolecular architecture while maintaining low polydispersities[1]. A development that is directly related to the subject of this review concerns the 'living' free-radical polymerization of macromonomers leading to well-defined graft copolymers[2]. Using conventional free-radical techniques, Tsukahara *et al.*[3] succeeded in polymerizing macromonomers, obtained by anionic polymerization, consisting of oligostyrene side chains ($700 \leq M_n \leq 5000\,g\,mol^{-1}$) and a high molar mass polymethacrylate main chain. In this way highly branched flexible chains, that is, molecular bottlebrushes, were obtained. An exciting possibility, which is to some extent responsible for the current interest, is the possibility that the presence of a large number of sufficiently long side chains might induce enough rigidity to induce lyotropic behaviour in suitable solvents. This rigidity is directly related to the solvent quality. If the solvent is a good solvent for the side chains, the side chains will repel each other, leading to an extended bottlebrush conformation.

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This prospect becomes even more interesting once it is realized that bottlebrush structures can be obtained in a straightforward manner by noncovalent bonding between polymers and end-functionalized oligomers. It is even possible to imagine applications where the side chains are removed again after processing the lyotropic solution[4]. This is, however, not the only reason for the current upsurge in activity. The very well-ordered microphase-separated structures that might occur in the melt state are equally interesting both from a scientific viewpoint (for example, how does the reversibility of the side-chain bonding interfere with the phase behaviour?) as well as in relation to practical applications.

The synthesis of polymer structures by physical means (supramolecular chemistry) is a recent development. It has been applied extensively in the area of polymer liquid crystals, where monofunctional, low molar mass mesogens are complexed to polymers possessing complementary groups[5–7]. From this it is only a small step to bottlebrush structures, which by definition involve much longer flexible side chains. They have been prepared by ionic means, polyelectrolyte–surfactant complexes[8,9], and by hydrogen bonding between homopolymers and end-functionalized oligomers[10]. Along the same lines, various other structures have been 'synthesized'. Among these are diblock copolymer structures involving hydrogen bonding between telechelic polymers[11] and, the ultimate limit, linear chain molecules obtained by multiple hydrogen bonding between successive monomers[12].

Here we will concentrate on bottlebrush structures and indicate where the reversibility of the noncovalent side-chain attachment plays an important role and where it is inconsequential. Two extreme cases will be discussed separately: dilute solutions of bottlebrushes and concentrated solutions, including the solvent-free situation. In the first case the possibility that individual bottlebrushes adopt a rod-like conformation as a result of immersion in a good solvent for the side chains will be considered. In the opposite limit, the bottlebrushes strongly interact and self-assembled structures are obtained owing to the block copolymer nature of the molecules.

Lyotropic behaviour of molecular bottlebrushes

The conformation of molecular bottlebrushes in dilute solution is directly related to the solvent quality. In a good solvent for the side chains (although not necessarily for the backbone), the monomers of the side chains strongly repel each other. Consequently, the polymer backbone is stretched and a more extended conformation is formed. In this regime, the precise nature of the side-chain attachment (covalent or noncovalent) is relatively unimportant. It is well-known that lyotropic behaviour of semiflexible

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chains is only possible if the ratio λ/D between the persistence length λ and the diameter D of the chain molecule is sufficiently large, say of the order of ten or more[13]. The persistence length represents the characteristic length over which a chain section remains straight. Figure 1 presents a typical snapshot of a bottlebrush conformation obtained by Monte Carlo computer simulations[14]. Here the polymer chain consists of a main chain of 100 beads having 50 side chains of 20 beads each. All beads are freely jointed together, have equal size and are treated as hard spheres. The only constraint is the non-overlapping condition, which corresponds to an athermal solvent condition. In the figure the diameter D is indicated, which demonstrates its close relation with the average end-to-end distance of the side chains. Until very recently, no experimental evidence supporting lyotropic behaviour of highly branched flexible polymers could be found in the literature[15]. Theoretically, there is agreement on the qualitative statements that both λ and D increase with the side-chain length M; however, opinions vary considerably as far as the ratio λ/D is concerned. One school[4] claims a steady increase with M ($\lambda/D \sim M^{9/8}$), whereas another group[16] predicts it to be independent of the side-chain length ($\lambda/D \sim M^{0}$). In the former case, this ratio can always be made to satisfy the above-mentioned criterion for lyotropic behaviour ($\lambda/D > 10$) by selecting sufficiently long side chains. However, if the ratio is independent of the side-chain length, lyotropic behaviour may still be possible but will then depend on the precise chemical nature of the polymer backbone and the side chains. Experimentally, claims for lyotropic behaviour of polymacromonomers consisting of oligostyrene side chains ($700 \leq M_n \leq 5000\ \mathrm{g\,mol^{-1}}$) and a high molar mass polymethacrylate main chain have only recently been published[17,18]. A solution in toluene of these bottlebrushes exhibited a very narrow X-ray scattering peak at concentrations of 30 wt% and higher. In addition, multidetectional GPC, consisting of a multiangle light-scattering detector and a viscosity detector, was used to characterize the conformational characteristics of these polymacromonomers in dilute solution and demonstrate the induced rigidity, reflected in a large persistence length ($\lambda \approx 100$ nm). The experimental data show unambiguously the occurrence of ordered hexagonal structures in semidilute solution.

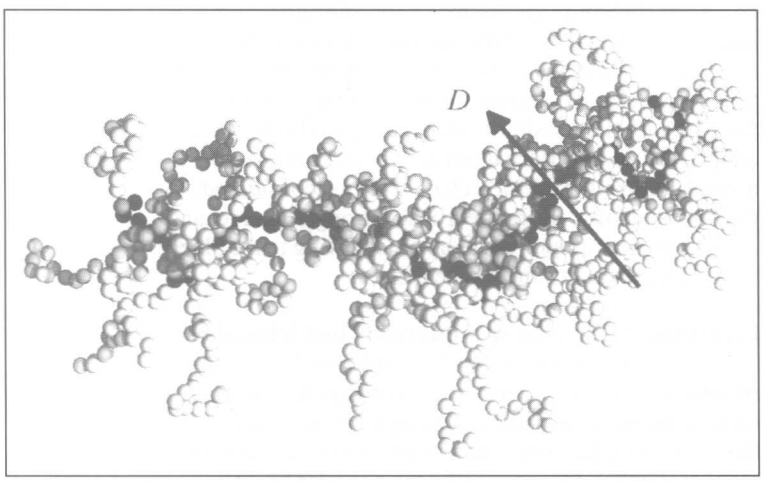

Fig. 1 *Characteristic bottlebrush conformation of a main chain of 100 beads and 50 side chains of 20 beads each. All beads have equal size and are freely jointed together. The only interactions are excluded-volume hard-sphere interactions. This corresponds to a bottlebrush in dilute athermal solution. Black molecules represent the backbone,* D *represents the diameter. (Reproduced, with permission, from Ref. 14.)*

Nevertheless, the connection with the lyotropic behaviour of semiflexible polymers is not completely clear. To illustrate this we will approach the problem from the opposite side, that is, starting from the melt. It is well known, and we will consider this in some detail in the next section, that block copolymers form microphase-separated structures in the melt[19], and bottlebrush polymers are no exception. Consequently, the addition of solvent to the microphase-separated melt state will first start to swell the structure. Only for a considerable amount of added solvent will a disordered solution be formed. An explicit example can be found in Ref. 20, dealing with bottlebrushes obtained by polyelectrolyte complexation between poly(4-vinylpyridine) (P4VP) and dodecyl benzene sulfonic acid. There the ordered state disappeared only when at least 50 wt% of xylene was added. However, the polymacromonomers considered by Wintermantel *et al.*[17,18] differ from these structures by the fact that they contain only an extremely small fraction of backbone material, of the order of 1–2 wt%. Thus, the structures can, to a good approximation, be considered as consisting of pure polystyrene only, with a very dense almost globular core and a much less dense corona. In this case a block-copolymer-like order–disorder transition should not be expected. Because the good solvent induces an effective repulsion between the coronas, a characteristic length of the order of the diameter of the polymacromonomers is present. The concentration of 30 wt% in toluene corresponds to the critical overlap concentration and the intermolecular repulsion results in a sharp Bragg reflection. From the limited number of experimental results available, it is obviously very difficult to conclude anything about the behaviour of λ/D as a function of M.

An alternative approach to this problem is by computer simulations, through which the conformational characteristics of isolated molecular bottlebrushes can be studied exactly. Figure 1 presents a snapshot of such a study[14]. This indicated that although the persistence length and the diameter of the structures increase with the side-chain length their ratio remained constant at best (actually, a slight decrease was even observed). Moreover, the ratio λ/D turned out to be much smaller than ten, suggesting that, in general, lyotropic behaviour for bottlebrush structures cannot be explained in the same way as for semiflexible homopolymers. Usually, it will be more directly related to the microphase separation in block copolymer systems. In all cases, the density near the backbone will be rather high, which may severely limit the number of backbones that can aggregate. This is confirmed by the results of Antonietti and Conrad[21], who observed a cylindrical mesophase in the solid polyelectrolyte–surfactant complex consisting of poly(acrylic acid) and dodecyltrimethylammonium counter-ions. It was estimated that in this case each cylinder consists on average of only four polyelectrolyte chains.

Order–disorder transitions

So far, molecular bottlebrushes in solution have been considered. Their melt state is equally interesting, in particular in the case of noncovalent side-chain bonding. The case of polyelectrolyte–surfactant complexes has been

studied in detail by Antonietti *et al.*[8,9] Here we will concentrate on bottlebrushes obtained by hydrogen bonding between end-functionalized oligomers and homopolymers. The most extensively studied system consists of P4VP and pentadecylphenol (PDP)[22–24]. The hydrogen bonding between the basic nitrogen of the pyridine ring and the OH of the phenol group is very strong. Figure 2 presents a schematic picture of a P4VP–PDP bottlebrush. For an excess of pyridine groups relative to the phenol groups and at not too high a temperature, nearly all PDP molecules are hydrogen bonded to P4VP and the system resembles, in many ways, bottlebrushes involving only covalent bonds. There are, however, essential differences. Because the bonding is reversible, thermodynamics will decide the location of the side chains along the backbone. Computer simulations indicate that, at least under certain conditions, the location of the side chains is uncorrelated and that the number of molecules with a given number of side chains satisfies a binomial distribution[25]. In addition, no experimental indications for cooperative hydrogen bonding have been found, which is in clear contrast to polyelectrolyte–surfactant complexation[9,22]. Microphase separation behaviour is found to occur for a comparable number of phenol and pyridine groups, a situation that will be addressed first. In the limit of a large excess of either component, macrophase separation between a microphase-separated and a homogeneous phase might occur as well. This will be considered in the subsequent section.

Order–disorder transitions in pure P4VP–PDP$_x$ (where x represents the ratio between the number of PDP molecules and the number of pyridine groups), from a homogeneous high-temperature state to a microphase-separated low-temperature lamellar state (schematically illustrated in Fig. 2), were first observed only recently[23,24]. The transition temperature depends on the precise value of x. For $x \approx 1$, the transition occurs at approximately 70°C, as observed by X-ray measurements as well as by dynamic mechanical spectroscopy. Figure 3 presents X-ray spectra obtained at the Synchrotron Radiation Source at Daresbury, UK[23,24]. At elevated temperatures a characteristic scattering peak at finite non-zero angle is already present. As is now well known, this kind of peak is characteristic of the block copolymer nature of the constituents. It is present in the homogeneous state owing to concentration fluctuations, reflecting the so-called correlation hole effect[25,26]. The transition from this homogeneous state to a microphase-separated state is accompanied by a spectacular increase in the scattering peak at approximately the same angle. In the case of P4VP–PDP$_{1.0}$ it is a transition to a lamellar structure. As for ordinary block copolymers, several other structures are in principle possible but require side chains of a different length. The rheological properties of block copolymer systems are also strongly affected by an order–disorder transition[27]. For a transition to a lamellar structure in ordinary diblock copolymers the behaviour of the dynamic moduli G' and G'', as a function of frequency ω, crosses over from a liquid-like behaviour ($G' \sim \omega^{2.0}$ and $G'' \sim \omega$) to a response intermediate between a Newtonian fluid and a solid ($G' \approx G'' \sim \omega^{0.5}$). Figure 4 demonstrates that the P4VP–PDP$_{1.0}$ bottlebrush system behaves in an analogous manner[24]. Figure 2b presents a cartoon of the local structure[24,28]. The fact that the

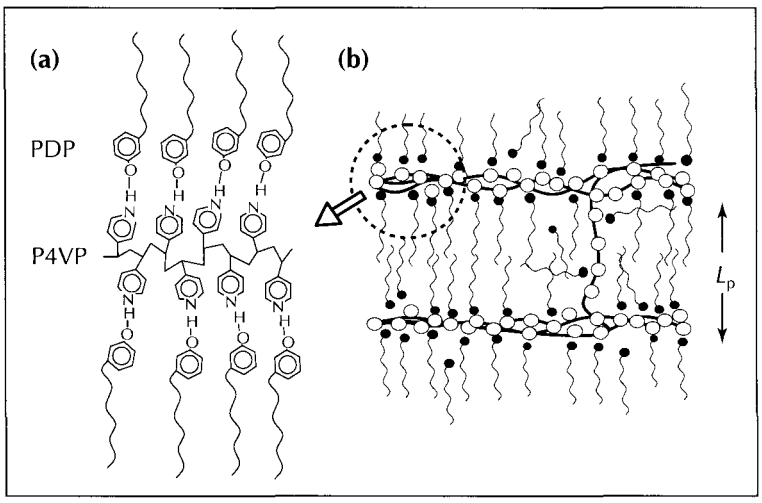

Fig. 2 *Schematic illustration of* ***(a)*** *P4VP–PDP hydrogen bonding and* ***(b)*** *the corresponding microphase-separated lamellar structure with a long period,* L_p. *(Reproduced, with permission, from Ref. 24.)*

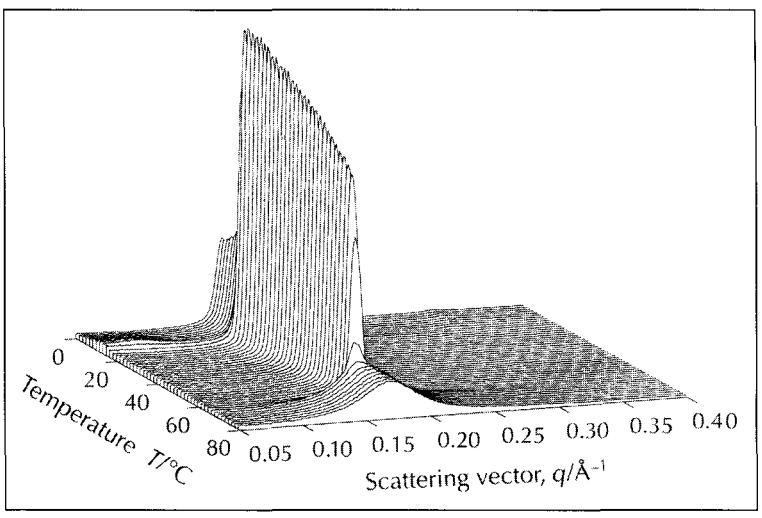

Fig. 3 *Small-angle X-ray spectra of P4VP–PDP$_{0.85}$ as a function of temperature, measured during slow cooling at 5°C min^{-1} from the melt at 100°C; q represents the scattering vector. The order–disorder transition from a homogeneous state to a microphase-separated state occurs at about 65°C and is accompanied by a strong increase in scattering. The transition at 25°C corresponds to the side-chain crystallization. (Reproduced, with permission, from Ref. 23.)*

side-chain bonding is reversible facilitates the formation of highly ordered structures. On average, the side chains simply occupy positions that comply best with the microphase-separated structure. Polyelectrolyte–surfactant complexes behave differently to the extent that there the complexation is highly cooperative, following a 1:1 stoichiometry. As a consequence, molecular packing constraints result in a cascade of modifications to the principal morphology, such as undulated lamellae and 'egg-carton' phases[29].

Phase diagram for mixtures of homopolymers and end-functionalized oligomers

Finally, the phase diagram for the general case of mixtures of end-functionalized oligomers and suitable homopolymers will be considered. The phase behaviour in associating block copolymer systems has been addressed theoretically by Tanaka and Ishida[30,31]. The analysis starts by addressing the homogeneous high-temperature state,

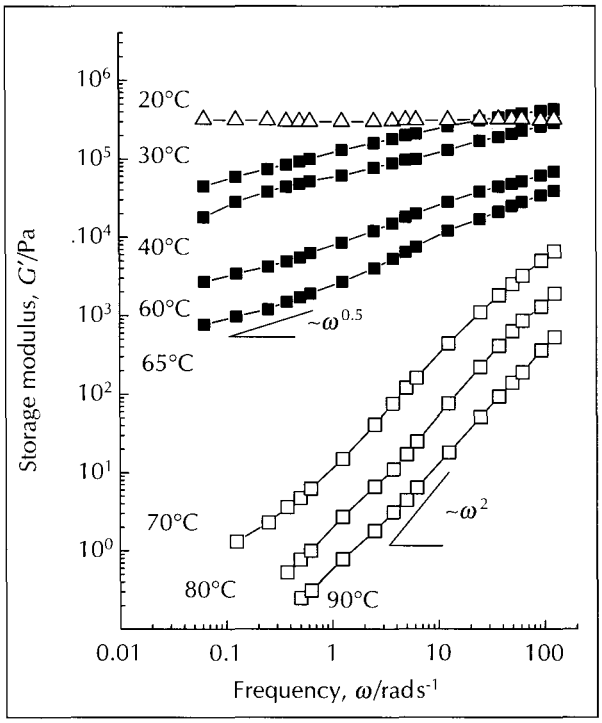

Fig. 4 *Isothermal frequency (ω) scans of the dynamic storage modulus G′ of P4VP– $PDP_{1.0}$ at various temperatures. The crossover from a liquid-like behaviour (G′ ~ $\omega^{2.0}$) to a response (G′ ~ $\omega^{0.5}$) intermediate between a Newtonian fluid (G′ ~ ω) and a solid (G′ ~ ω^0) occurs around 65 °C. (Reproduced, with permission, from Ref. 24.)*

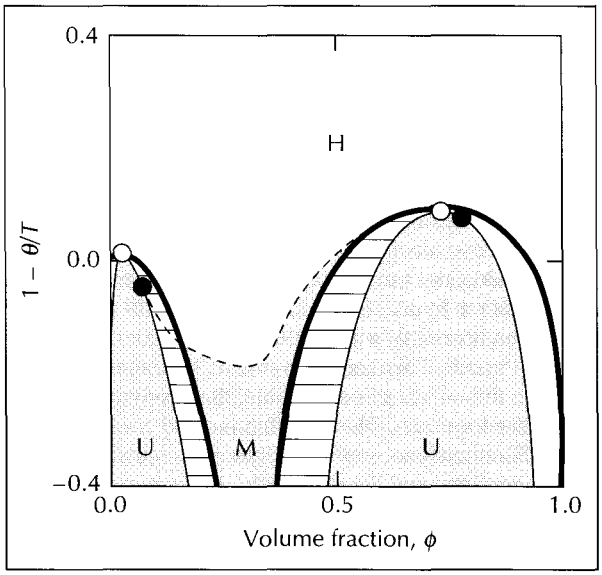

Fig. 5 *Characteristic phase diagram for mixtures of homopolymers and end-functionalized oligomers that can form hydrogen bonds with the homopolymers. The term φ denotes the volume fraction of oligomers and θ represents the theta temperature for mixtures of the oligomers and homopolymers if no functional endgroups were present. The binodal (thick solid line), the spinodals (solid borderlines of shaded areas), microphase-separation transition line (dashed line), critical solution points (○) and Lifshitz points (●) are shown. The homogeneous mixture region, microphase separation region and macroscopically unstable regions are indicated by* H, M *and* U, *respectively. The horizontal-line fill indicates a microphase-separated state. (Reproduced, with permission, from Ref. 31.)*

determining first the distribution function describing the different bottlebrush structures formed by the hydrogen bonding equilibrium. Next, the Random Phase Approximation[26] is used to calculate the correlation functions and to determine the stability limits as well as the nature (macro or micro) of the phase transition. Because it is only the functional head of the oligomer that can interact favourably with the homopolymer, it is not hard to understand that an excess of either component might give rise to macrophase separation. For the same reason, microphase separation will occur at near-stoichiometric amounts of complementary groups. The point that separates or connects micro- and macrophase separation is called a Lifshitz point and the phase diagram will, in general, contain two of these points, one at either side of the diagram. Macrophase separation can be into two homogeneous states, into a homogeneous and a microphase-separated phase or even into two different microphase-separated states. It is precisely here that the reversibility of the hydrogen bonding is of utmost importance because it allows the redistribution of side chains between the two phases. The average structure, and in particular the average number of side chains per bottlebrush, may differ considerably between the two phases in equilibrium. One possible phase diagram, delineating the stability limits, is presented in Fig. 5. The binodals for the equilibrium between the homogeneous phase and the microphase-separated phase are only an approximation. The precise microphase-separated morphologies, and thus the free energies, are not known yet. Presumably, the apparent universal character of self-assembly, manifested in a sequence of structures from lamellar to hexagonal to body-centred cubic, should also be present here. However, the possibility of redistribution of side chains over the phases involved presents an essential new element that has not been considered. Consequently, this is as far as the theory has been developed. Further progress requires an exact analysis of the nature of the microphases. Macrophase separation has been observed in the P4VP–PDP system for an excess of PDP[24] but a detailed experimental study has not been performed so far.

Future prospects

Theoretically and experimentally, the exploration of ordered structures in systems containing bottlebrushes has only just begun. The role of excluded-volume interactions between the side chains by the formation of lyotropic solutions of bottlebrushes is still open to debate. Computer simulation studies of much larger structures than the ones reported here are not feasible in the foreseeable future. Therefore, the answer may well have to come from systematic studies of dilute solutions of polymacromonomers as a function of both side-chain and backbone length. This issue is relatively unrelated to the way these structures are prepared. For the phase behaviour in the absence of solvent this is certainly not the case and at least three essentially different systems can be distinguished: bottlebrushes involving only covalent bonds, polyelectrolyte–surfactant complexes and those obtained by hydrogen bonding between end-functionalized oligomers and homopolymers. The characteristic difference between the last two is the highly cooperative nature of complexation in the former case. Its consequences have been discussed extensively by Antonietti *et al.*[9] Here we focused on the latest results for the hydrogen bonding system and showed the presence of order–disorder transitions. In contrast to the polyelectrolyte–surfactant

systems, only a lamellar morphology has been observed so far. It remains to be seen whether this predominant morphology is due to the particular oligomer length used or if it is somehow connected to the reversibility of the hydrogen bonding. In any event, a detailed theoretical analysis and experiments involving longer phenolalkyl chains are called for. Both are presently being vigorously pursued in our groups.

Although various applications of these systems are possible, there is at least one area where the use of end-functionalized alkyl oligomers has already been extensively explored. This concerns blends of polymer–amphiphile complexes with another polymer. In this case, compatibilized ternary structures might be obtained '*in situ*', as indicated by observations in blends of electrically conducting polymers with polyolefins[32]. Clearly, the concepts discussed in this review offer exciting possibilities for molecular engineering of self-organized structures.

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References

1 Georges, M.K., Veregin, R.P.N., Kazmaier, P.M. and Hamer, G.K. (1994) *Trends Polym. Sci.* 2, 66
2 Hawker, C.J. *et al.* (1997) *Macromol. Chem. Phys.* 198, 155
3 Tsukahara, Y., Tsutsumi, K., Yamashita, S. and Shimada, S. (1990) *Macromolecules* 23, 5201
4 Fredrickson, G.H. (1993) *Macromolecules* 26, 2825
5 Brandys, F.A. and Bazuin, C.G. (1996) *Chem. Mater.* 8, 83
6 Imrie, C.T. (1995) *Trends Polym. Sci.* 3, 22
7 Kato, T., Kihara, H., Ujiie, S., Uryu, T. and Fréchet, J.M.J. (1996) *Macromolecules* 29, 8734
8 Antonietti, M., Conrad, J. and Thünemann, A. (1994) *Macromolecules* 27, 6007
9 Antonietti, M., Burger, C. and Thünemann, A. *Trends Polym. Sci.* 5 (in press)
10 Ruokolainen, J. *et al.* (1996) *Macromolecules* 29, 6621
11 Inomata, K., Haraguchi, M. and Nose, T. (1996) *Polymer* 37, 4223
12 Lehn, J-M. (1995) *Supramolecular Chemistry*, VCH
13 Grosberg, A.Y. and Khokhlov, A.R. (1994) *Statistical Physics of Macromolecules*, AIP Press
14 Saariaho, M., Szleifer, I., Erukhimovich, I., Ikkala, O. and ten Brinke, G. *J. Chem. Phys.* (in press)
15 Platé, N.A. and Shibaev, V.P. (1987) *Comb-Shaped Polymers and Liquid Crystals*, Plenum Press
16 Birshtein, T.M., Borisov, O.V., Zhulina, Y.B., Khokhlov, A.R. and Yurasova, T.A. (1987) *Polym. Sci. USSR* 29, 1293
17 Wintermantel, M. *et al.* (1995) *Angew. Chem., Int. Ed. Engl.* 34, 1472
18 Wintermantel, M. *et al.* (1996) *Macromolecules* 29, 978
19 Bates, F.S. and Fredrickson, G.H. (1990) *Annu. Rev. Phys. Chem.* 41, 525
20 Ikkala, O., Ruokolainen, J., ten Brinke, G., Torkkeli, M. and Serimaa, R. (1995) *Macromolecules* 28, 7088
21 Antonietti, M. and Conrad, J. (1994) *Angew. Chem., Int. Ed. Engl.* 33, 1869
22 Ruokolainen, J., ten Brinke, G., Ikkala, O., Torkkeli, M. and Serimaa, R. (1996) *Macromolecules* 29, 3409
23 Ruokolainen, J., Torkkeli, M., Serimaa, R., Komanschek, B.E., Ikkala, O. and ten Brinke, G. (1996) *Phys. Rev. E* 54, 6646
24 Ruokolainen, J., Torkkeli, M., Serimaa, R., Komanschek, E., ten Brinke, G. and Ikkala, O. (1997) *Macromolecules* 30, 2002
25 Huh, J., Ikkala, O. and ten Brinke, G. (1997) *Macromolecules* 30, 1828
26 de Gennes, P.G. (1979) *Scaling Concepts in Polymer Physics*, Cornell University Press
27 Fredrickson, G.H. and Bates, F.S. (1996) *Annu. Rev. Mater. Sci.* 26, 501
28 ten Brinke, G., Ruokolainen, J. and Ikkala, O. (1996) *Europhys. Lett.* 35, 91
29 Antonietti, M., Wentzel, A. and Thünemann, A. (1996) *Langmuir* 12, 2111
30 Tanaka, F. (1996) *Adv. Colloid Interface Sci.* 63, 23
31 Tanaka, F. and Ishida, M. (1997) *Macromolecules* 30, 1836
32 Tanner, J., Ikkala, O., Laakso, J. and Passiniemi, P. (1996) *Mater. Res. Soc. Symp. Proc.* 413, 565 [*Electrical, Optical and Magnetic Properties of Organic Solid State Materials III*]

Forthcoming Trends

The topics that will be covered in forthcoming issues of *Trends in Polymer Science* include:

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- Stopped-flow techniques for olefin polymerization
- High osmotic pressure chromatography
- The role of viscoelastic properties in pressure-sensitive adhesives
- Polymers for immunoisolation
- Polycarbosilane-based liquid crystals
- Folding in polymer crystals and proteins
- Impact fracture in polymers
- Abiotic control of polymer degradation
- Blood-compatible polymers
- Laser scanning confocal microscopy
- Fluorescence spectroscopy of polymers
- The T_g of miscible polymers and copolymers
- Nucleic acid analogues
- Investigation of high-concentration polymer solutions